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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Cosmetic composition comprising coloured gloss pigments having at least one coating of SiO 0.03 to 0.95

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Cosmetic composition comprising coloured gloss pigments having at least one coating of $SiO_{0.03 \text{ to } 0.95}$

The present invention relates to a cosmetic preparation or formulation comprising

(a) from 0.0001 to 90 % by weight of a gloss pigment comprising

(a1) a core consisting of a substantially transparent or metallically reflecting material, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95

and

(b) from 10 to 99.9999 % of a cosmetically suitable carrier material, based on the total weight of the cosmetic preparation or formulation.

The preparations according to the invention are especially preparations or formulations that are suitable for making-up the lips or the skin and for colouring the hair or the nails.

The cosmetic preparations are, for example, lipsticks, blushers, foundations, nail varnishes and hair shampoos.

The gloss pigments may be used singly or in the form of mixtures. It is, in addition, possible to use the gloss pigments together with other pigments and/or colorants.

The cosmetic preparations and formulations according to the invention preferably contain the gloss pigment in an amount from 0.005 to 50 % by weight, based on the total weight of the preparation.

Suitable carrier materials for the cosmetic preparations and formulations according to the invention include the customary materials used in such compositions.

The cosmetic preparations and formulations according to the invention may be in the form of, for example, sticks, ointments, creams, emulsions, suspensions, dispersions, powders or solutions. They are, for example, lipsticks, mascara preparations, blushers, eye-shadows, foundations, eyeliners, powder or nail varnishes.

If the preparations are in the form of sticks, for example lipsticks, eye-shadows, blushers or foundations, the preparations consist for a considerable part of fatty components, which may consist of one or more waxes, for example ozokerite, lanolin, lanolin alcohol, hydrogenated lanolin, acetylated lanolin, lanolin wax, beeswax, candelilla wax, microcrystalline wax, carnauba wax, cetyl alcohol, stearyl alcohol, cocoa butter, lanolin fatty acids, petrolatum, petroleum jelly, mono-, di- or tri-glycerides or fatty esters thereof that are solid at 25°C, silicone waxes, such as methyloctadecane-oxypolysiloxane and poly(dimethylsiloxy)-stearoxysiloxane, stearic acid monoethanolamine, colophane and derivatives thereof, such

as glycol abietates and glycerol abietates, hydrogenated oils that are solid at 25°C, sugar glycerides and oleates, myristates, lanolates, stearates and dihydroxystearates of calcium, magnesium, zirconium and aluminium.

The fatty component may also consist of a mixture of at least one wax and at least one oil, in which case the following oils, for example, are suitable: paraffin oil, purcelline oil, perhydrosqualene, sweet almond oil, avocado oil, calophyllum oil, castor oil, sesame oil, jojoba oil, mineral oils having a boiling point about from 310 to 410°C, silicone oils, such as dimethylpolysiloxane, linoleyl alcohol, linolenyl alcohol, oleyl alcohol, cereal grain oils, such as wheatgerm oil, isopropyl lanolate, isopropyl palmitate, isopropyl myristate, butyl myristate, cetyl myristate, hexadecyl stearate, butyl stearate, decyl oleate, acetyl glycerides, octanoates and decanoates of alcohols and polyalcohols, for example of glycol and glycerol, ricinoleates of alcohols and polyalcohols, for example of cetyl alcohol, isostearyl alcohol, isocetyl lanolate, isopropyl adipate, hexyl laurate and octyl dodecanol.

The fatty components in such preparations in the form of sticks may generally constitute up to 99.91 % by weight of the total weight of the preparation.

The cosmetic preparations and formulations according to the invention may additionally comprise further constituents, such as, for example, glycols, polyethylene glycols, polypropylene glycols, monoalkanolamides, non-coloured polymeric, inorganic or organic fillers, preservatives, UV filters or other adjuvants and additives customary in cosmetics, for example a natural or synthetic or partially synthetic di- or tri-glyceride, a mineral oil, a silicone oil, a wax, a fatty alcohol, a Guerbet alcohol or ester thereof, a lipophilic functional cosmetic active ingredient, including sun-protection filters, or a mixture of such substances.

A lipophilic functional cosmetic active ingredient suitable for skin cosmetics, an active ingredient composition or an active ingredient extract is an ingredient or a mixture of ingredients that is approved for dermal or topical application. The following may be mentioned by way of example:

- active ingredients having a cleansing action on the skin surface and the hair; these include all substances that serve to cleanse the skin, such as oils, soaps, synthetic detergents and solid substances;
- active ingredients having a deodorising and perspiration-inhibiting action: they include antiperspirants based on aluminium salts or zinc salts, deodorants comprising bactericidal or bacteriostatic deodorising substances, for example triclosan, hexachlorophene, alcohols and cationic substances, such as, for example, quaternary ammonium salts, and odour absorbers, for example ®Grillocin (combination of zinc ricinoleate and various additives) or triethyl citrate (optionally in combination with an antioxidant, such as, for example, butyl hydroxytoluene) or ion-exchange resins;

- active ingredients that offer protection against sunlight (UV filters): suitable active ingredients are filter substances (sunscreens) that are able to absorb UV radiation from sunlight and convert it into heat; depending on the desired action, the following light-protection agents are preferred: light-protection agents that selectively absorb sunburn-causing high-energy UV radiation in the range of approximately from 280 to 315 nm (UV-B absorbers) and transmit the longer-wavelength range of, for example, from 315 to 400 nm (UV-A range), as well as light-protection agents that absorb only the longer-wavelength radiation of the UV-A range of from 315 to 400 nm (UV-A absorbers);
suitable light-protection agents are, for example, organic UV absorbers from the class of the p-aminobenzoic acid derivatives, salicylic acid derivatives, benzophenone derivatives, dibenzoylmethane derivatives, diphenyl acrylate derivatives, benzofuran derivatives, polymeric UV absorbers comprising one or more organosilicon radicals, cinnamic acid derivatives, camphor derivatives, trianilino-s-triazine derivatives, phenyl-benzimidazolesulfonic acid and salts thereof, menthyl anthranilates, benzotriazole derivatives, and/or an inorganic micropigment selected from aluminium oxide- or silicon dioxide-coated TiO_2, zinc oxide or mica;
- active ingredients against insects (repellents) are agents that are intended to prevent insects from touching the skin and becoming active there; they drive insects away and evaporate slowly; the most frequently used repellent is diethyl toluamide (DEET); other common repellents will be found in "Pflegekosmetik" (W. Raab and U. Kindl, Gustav-Fischer-Verlag Stuttgart/New York,1991) on page 161;
- active ingredients for protection against chemical and mechanical influences: these include all substances that form a barrier between the skin and external harmful substances, such as, for example, paraffin oils, silicone oils, vegetable oils, PCL products and lanolin for protection against aqueous solutions, film-forming agents, such as sodium alginate, triethanolamine alginate, polyacrylates, polyvinyl alcohol or cellulose ethers for protection against the effect of organic solvents, or substances based on mineral oils, vegetable oils or silicone oils as "lubricants" for protection against severe mechanical stresses on the skin;
- moisturising substances: the following substances, for example, are used as moisture-controlling agents (moisturisers): sodium lactate, urea, alcohols, sorbitol, glycerol, propylene glycol, collagen, elastin and hyaluronic acid;
- active ingredients having a keratoplastic effect: benzoyl peroxide, retinoic acid, colloidal sulfur and resorcinol;
- antimicrobial agents, such as, for example, triclosan or quaternary ammonium compounds;

- oily or oil-soluble vitamins or vitamin derivatives that can be applied dermally: for example vitamin A (retinol in the form of the free acid or derivatives thereof), panthenol, pantothenic acid, folic acid, and combinations thereof, vitamin E (tocopherol), vitamin F; essential fatty acids; or niacinamide (nicotinic acid amide);
- vitamin-based placenta extracts: active ingredient compositions comprising especially vitamins A, C, E, B_1, B_2, B_6, B_{12}, folic acid and biotin, amino acids and enzymes as well as compounds of the trace elements magnesium, silicon, phosphorus, calcium, manganese, iron or copper;
- skin repair complexes: obtainable from inactivated and disintegrated cultures of bacteria of the bifidus group;
- plants and plant extracts: for example arnica, aloe, beard lichen, ivy, stinging nettle, ginseng, henna, camomile, marigold, rosemary, sage, horsetail or thyme;
- animal extracts: for example royal jelly, propolis, proteins or thymus extracts;
- cosmetic oils that can be applied dermally: neutral oils of the Miglyol 812 type, apricot kernel oil, avocado oil, babassu oil, cottonseed oil, borage oil, thistle oil, groundnut oil, gamma-oryzanol, rosehip-seed oil, hemp oil, hazelnut oil, blackcurrant-seed oil, jojoba oil, cherry-stone oil, salmon oil, linseed oil, cornseed oil, macadamia nut oil, almond oil, evening primrose oil, mink oil, olive oil, pecan nut oil, peach kernel oil, pistachio nut oil, rape oil, rice-seed oil, castor oil, safflower oil, sesame oil, soybean oil, sunflower oil, tea tree oil, grapeseed oil or wheatgerm oil.

The preparations in stick form are preferably anhydrous but may in certain cases comprise a certain amount of water which, however, in general does not exceed 40 % by weight, based on the total weight of the cosmetic preparation.

If the cosmetic preparations and formulations according to the invention are in the form of semi-solid products, that is to say in the form of ointments or creams, they may likewise be anhydrous or aqueous. Such preparations and formulations are, for example, mascaras, eyeliners, foundations, blushers, eye-shadows, or compositions for treating rings under the eyes.

If, on the other hand, such ointments or creams are aqueous, they are especially emulsions of the water-in-oil type or of the oil-in-water type that comprise, apart from the pigment, from 1 to 98.8 % by weight of the fatty phase, from 1 to 98.8 % by weight of the aqueous phase and from 0.2 to 30 % by weight of an emulsifier.

Such ointments and creams may also comprise further conventional additives, such as, for example, perfumes, antioxidants, preservatives, gel-forming agents, UV filters, colorants, pigments, pearlescent agents, non-coloured polymers as well as inorganic or organic fillers.

If the preparations are in the form of a powder, they consist substantially of a mineral or inorganic or organic filler such as, for example, talcum, kaolin, starch, polyethylene powder or polyamide powder, as well as adjuvants such as binders, colorants etc..

Such preparations may likewise comprise various adjuvants conventionally employed in cosmetics, such as fragrances, antioxidants, preservatives etc..

If the cosmetic preparations and formulations according to the invention are nail varnishes, they consist essentially of nitrocellulose and a natural or synthetic polymer in the form of a solution in a solvent system, it being possible for the solution to comprise other adjuvants, for example pearlescent agents.

In that embodiment, the coloured polymer is present in an amount of approximately from 0.1 to 5 % by weight.

The cosmetic preparations and formulations according to the invention may also be used for colouring the hair, in which case they are used in the form of shampoos, creams or gels that are composed of the base substances conventionally employed in the cosmetics industry and a pigment according to the invention.

The cosmetic preparations and formulations according to the invention are prepared in conventional manner, for example by mixing or stirring the components together, optionally with heating so that the mixtures melt.

The gloss pigment generally comprises

(a1) a core consisting of a substantially transparent or metallically reflecting material, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95.

The gloss pigment preferably has the following layer structure:

(a3) SiO_2,

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95,

(a1) a core consisting of a substantially transparent or metallically reflecting material, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95,

(a3) SiO_2;

or

(a4) a coating consisting of any solid material, the composition of which differs from that of the coating (a3),

(a3) SiO_2,

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95,

(a1) a core consisting of a substantially transparent or metallically reflecting material, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95,

(a3) SiO_2,

(a4) a coating consisting of any solid material, the composition of which differs from that of the coating (a3).

If the core consists of a metallically reflecting material, that material is preferably selected from Ag, Al, Au, Cu, Cr, Ge, Mo, Ni, Si, Ti, Zn, alloys thereof, graphite, Fe_2O_3 and MoS_2. Special preference is given to Al.

If the core consists of a transparent material, the material is preferably selected from mica, SiO_z, in particular SiO_2 and SiO_2/TiO_2 mixtures, in particular SiO_2/TiO_2 mixtures. Special preference is given to SiO_z, wherein $1.4 \leq z \leq 2.0$.

The material of coating (a4) is advantageously a metal oxide, such as, for example, TiO_2, ZrO_2, SiO, SiO_2, SnO_2, GeO_2, ZnO, Al_2O_3, V_2O_5, Fe_2O_3, Cr_2O_3, $PbTiO_3$ or CuO, or a mixture thereof.

The metal oxide layers are preferably applied by a wet-chemical method, in which context it is possible to employ the wet-chemical coating techniques developed for the preparation of pearl lustre pigments; techniques of this kind are described, for example, in DE 14 67 468, DE 19 59 988, DE 20 09 566, DE 22 14 545, DE 22 15 191, DE 22 44 298, DE 23 13 331, DE 25 22 572, DE 31 37 808, DE 31 37 809, DE 31 51 343, DE 31 51 354, DE 31 51 355, DE 32 11 602, DE 32 35 017, or else in further patent documents and other publications.

For coating, the substrate particles are suspended in water, and one or more hydrolysable metal salts are added at a pH which is appropriate for hydrolysis and is chosen such that the metal oxides and/or metal oxide hydrates are precipitated directly onto the particles without any instances of secondary precipitation. The pH is kept constant usually by simultaneous metered addition of a base or alkali. The pigments are subsequently separated off, washed and dried and, if desired, calcined, the calcination temperature possibly being optimized in respect of the particular coating. If desired, following the application of individual coatings the

pigments can be separated off, dried and, if desired, calcined before being resuspended for the application of further layers by precipitation (cf. US-A-6,132,873).

In a preferred embodiment, the gloss pigment has the following layer structure: $SiO_2/SiO_x/SiO_z/SiO_x/SiO_2$, $SiO_2/SiO_x/Al/SiO_x/SiO_2$, $TiO_2/SiO_2/SiO_x/SiO_z/SiO_x/SiO_2/TiO_2$ or $TiO_2/SiO_2/SiO_x/Al/SiO_x/SiO_2/TiO_2$, wherein x is from 0.03 to 0.95 and $0.95 < z \leq 2.0$, with gloss pigments having the following layer structure $SiO_2/SiO_x/SiO_z/SiO_x/SiO_2$ or $TiO_2/SiO_2/SiO_x/SiO_z/SiO_x/SiO_2/TiO_2$ being novel.

The present invention accordingly relates also to gloss pigments having the following layer structure
$SiO_2/SiO_x/SiO_z/SiO_x/SiO_2$, or
$TiO_2/SiO_2/SiO_x/SiO_z/SiO_x/SiO_2/TiO_2$,
wherein x is from 0.03 to 0.95, preferably from 0.05 to 0.3, and $0.95 < z \leq 2.0$, preferably $1.4 \leq z \leq 2.0$.

The gloss pigments are generally particles having a length of from 2 µm to 5 mm, a width of from 2 µm to 2 mm, and a thickness of from 20 nm to 1.5 µm, and a ratio of length to thickness of at least 2:1, the particles having a core of SiO_z having two substantially parallel faces, the distance between which is the shortest axis of the core, and an SiO_x layer applied to those parallel faces, and, optionally, further layers. The further layers may be applied to the parallel faces or to the entire surface.

The core is a platelet having an average diameter of from 1 to 50 µm and a thickness of from 20 to 500 nm.
The thickness of the SiO_x layer is generally from 5 to 200 nm, preferably from 5 to 100 nm.
The thickness of the SiO_z layer is generally from 1 to 200 nm, preferably from 2 to 100 nm.
The thickness of the TiO_2 layer is generally from 1 to 200 nm, preferably from 10 to 150 nm.

By using the gloss pigments according to the invention in cosmetics it is possible to obtain cosmetics whose colour changes in dependence upon the viewing angle ("flop effect"). In particular, the gloss pigments not having the TiO_2 coating, which consist only of silicon and oxygen, are, by virtue of the fact that they are free of heavy metals, outstandingly suitable for cosmetic applications.

The SiO_x, SiO_z, SiO_2 and TiO_2 layers arranged mirror-symmetrically with respect to the core of Al, SiO_z preferably have the same layer thickness. In a further embodiment of the invention, the carrier layer may be surrounded on both sides by metal oxides having different layer thicknesses.

The SiO_y substrates in the form of platelets or the plane-parallel structures of SiO_y, wherein $0.95 < y \leq 1.8$, preferably wherein $1.0 \leq y \leq 1.5$, are obtained by a method comprising the following steps:

a) vapour-deposition of a separating agent onto a (movable) carrier to produce a separating agent layer,

b) vapour-deposition of an SiO_X layer onto the separating agent layer ($0.03 < x \leq 0.95$),

c) vapour-deposition of an SiO_y layer ($0.95 < y \leq 1.8$) onto the SiO_x layer obtained in step b),

d) vapour-deposition of an SiO_X layer ($0.03 < x \leq 0.95$) onto the SiO_y layer obtained in step c),

e) dissolution of the separating agent layer in a solvent,

f) separation of the gloss pigment from the solvent,

the SiO_y layer in step c) being vapour-deposited from a vaporiser containing a charge comprising a mixture of Si and SiO_2, SiO_y or a mixture thereof, and

the SiO_x layer being vapour-deposited from a vaporiser charged with silicon.

The method indicated above makes available gloss pigments which, compared to natural mica effect pigments as well as to effect pigments produced in wet procedures, have a high degree of plane parallelism and a defined thickness in the range of ± 10 %, preferably ± 5 %, of the average thickness.

The separating agent condensed onto the carrier may be a lacquer, a polymer, such as, for example, the thermoplastic polymers described in US-B-6,398,999, an organic substance soluble in organic solvents or water and vaporisable *in vacuo*, such as anthracene, anthraquinone, acetamidophenol, acetylsalicylic acid, camphoric anhydride, benzimidazole, benzene-1,2,4-tricarboxylic acid, biphenyl-2,2-dicarboxylic acid, bis(4-hydroxyphenyl)sulfone, dihydroxyanthraquinone, hydantoin, 3-hydroxybenzoic acid, 8-hydroxyquinoline-5-sulfonic acid monohydrate, 4-hydroxycoumarin, 7-hydroxycoumarin, 3-hydroxynaphthalene-2-carboxylic acid, isophthalic acid, 4,4-methylene-bis-3-hydroxynaphthalene-2-carboxylic acid, naphthalene-1,8-dicarboxylic anhydride, phthalimide and its potassium salt, phenolphthalein, phenothiazine, saccharin and its salts, tetraphenylmethane, triphenylene, triphenylmethanol or a mixture of at least two of those substances. The separating agent is preferably an

inorganic salt soluble in water and vaporisable *in vacuo* (see, for example, DE 198 44 357), such as sodium chloride, potassium chloride, lithium chloride, sodium fluoride, potassium fluoride, lithium fluoride, calcium fluoride, sodium aluminium fluoride and disodium tetraborate.

The SiO_y layer is obtained by heating a preferably stoichiometric mixture of fine silicon and quartz (SiO_2) powder in a vaporiser, which is described, for example, in DE 4342574 C1 and in US 6 202 591, to more than 1300°C under a high vacuum. The reaction product is silicon monoxide gas, which under vacuum is directed directly onto the passing carrier, where it condenses as SiO. Non-stoichiometric mixtures may also be used. The vaporiser contains a charge comprising a mixture of Si and SiO_2, SiO_y, or a mixture thereof, the particle size of the substances that react with one another (Si and SiO_2) being advantageously less than 0.3 mm. The weight ratio of Si to SiO_2 is advantageously in the range from 0.15:1 to 0.75:1 (parts by weight); preferably, a stoichiometric mixture is present. SiO_y present in the vaporiser vaporises directly. Si and SiO_2 react at a temperature of more than 1300°C to form silicon monoxide vapour.

In accordance with the invention, step e) is carried out at a pressure that is higher than the pressure in steps a) to d) and lower than atmospheric pressure.

The (movable) carrier preferably comprises one or more continuous metal belts, with or without a polymer coating, or one or more polyimide or polyethylene terephthalate belts. The (movable) carrier may furthermore comprise one or more discs, cylinders or other rotationally symmetrical bodies, which rotate about an axis.

The gloss pigments are separated from the solvent of the separating agent preferably by washing-out and subsequent filtration, sedimentation, centrifugation, decanting or evaporation. Furthermore, the gloss pigments may, after washing-out of the dissolved separating agent contained in the solvent, be frozen together with the solvent and subsequently subjected to a process of freeze-drying, whereupon the solvent is separated off as a result of sublimation below the triple point and the dry product remains behind in the form of individual plane-parallel structures.

The silicon suboxide condensed on the movable carrier starting from vaporised SiO corresponds to the formula SiO_y wherein $0.95 < y \leq 1.8$, preferably wherein $1.1 \leq y \leq 1.5$, y values of less than 1 being obtained by means of an excess of silicon in the vaporiser material. Except under an ultra-high vacuum, in industrial vacuums of a few 10^{-2} Pa

vaporised SiO always condenses as SiO_y wherein $1 \leq y \leq 1.8$, especially wherein $1.1 \leq y \leq 1.5$, because high-vacuum apparatuses always contain, as a result of gas emission from surfaces, traces of water vapour which react with the readily reactive SiO at vaporisation temperature. The SiO_y layers can be converted into $SiO_{1.8-2}$ layers by means of oxidative heat treatment.

If, under industrial vacuums of a few 10^{-2} Pa, Si is vaporised instead of SiO, silicon oxides are obtained which have a less-than-equimolar oxygen content, that is to say SiO_x wherein $0.03 \leq x \leq 0.90$, especially $0.05 \leq x \leq 0.5$, very especially $0.1 \leq x \leq 0.3$, which have astonishingly high stability to oxidation along with a high refractive index, even in thin layers. Heating in the presence of oxygen at from 150 to 500°C, preferably from 175 to 300°C, unexpectedly results in a very thin, e.g. approximately 20 nm thick, superficial silicon dioxide layer, which represents a very convenient method of producing structures having the layer sequence $SiO_2/SiO_x/SiO_2/SiO_x/SiO_2$. If thicker silicon dioxide layers are desired, they may conveniently be produced, as described above, by means of vapour-deposition of SiO_y and oxidative heat treatment thereof.

In detail, a salt, for example NaCl, followed successively by the layers of SiO_x and SiO_y, is vapour-deposited onto a carrier, which may be a continuous metal belt, passing by way of the vaporisers under a vacuum of <0.5 Pa, the vapour-deposited thicknesses of salt being about from 20 to 100 nm, preferably from 30 to 60 nm. On its further course, the belt-form carrier, which is closed to form a loop, runs through dynamic vacuum lock chambers of known mode of construction (cf. US 6 270 840) into a region of from 1 to 5×10^4 Pa pressure, preferably from 600 to 10^9 Pa pressure, and especially from 10^3 to 5×10^3 Pa pressure, where it is immersed in a dissolution bath. The temperature of the solvent should be so selected that its vapour pressure is in the indicated pressure range. With mechanical assistance, the separating agent layer rapidly dissolves and the product layer breaks up into flakes, which are then present in the solvent in the form of a suspension. On its further course, the belt is dried and freed from any contaminants still adhering to it. It runs through a second group of dynamic vacuum lock chambers back into the vaporisation chamber, where the process of coating with separating agent and product layer is repeated.

The suspension then present in both cases, comprising product structures and solvent, and the separating agent dissolved therein, is then separated in a further operation in accordance with a known technique. For that purpose, the product structures are first concentrated in the liquid and rinsed several times with fresh solvent in order to wash out the dissolved

separating agent. The product, in the form of a solid that is still wet, is then separated off by filtration, sedimentation, centrifugation, decanting or evaporation.

After drying, the product can be subjected to oxidative heat treatment, in which SiO_y is converted to $SiO_{1.8-2}$. Known methods are available for that purpose. Air or some other oxygen-containing gas is passed through the plane-parallel structures, which are in the form of loose material or in a fluidised bed, for several hours at a temperature of more than 200°C, preferably more than 400°C and especially from 500 to 1000°C. The product can then be brought to the desired particle size by means of grinding or air-sieving and delivered for further use.

It is possible to arrange several separating agent and product vaporisers one after the other in the running direction of the belt in the vaporisation zone. By that means there is obtained, with little additional outlay in terms of apparatus, a layer sequence of S + P + S + P, wherein S is the separating agent layer and P is the product layer. If the number of vaporisers is doubled and the belt speed is the same, twice the amount of product is obtained.

Separating off the plane-parallel structures after washing-out at atmospheric pressure can be carried out under gentle conditions by freezing the suspension, which has been concentrated to a solids content of about 50 %, and subjecting it in known manner to freeze-drying at about -10°C and 50 Pa pressure. The dry substance remains behind as product, which can be subjected to the steps of further processing by means of coating or chemical conversion.

Instead of using a continuous belt, it is possible to produce the product by carrying out the steps of vapour-deposition of separating agent and SiO, of dissolution, and of drying the carrier, in an apparatus having a rotary body, in accordance with DE-A-199 52 032. The rotary body may be one or more discs, a cylinder or any other rotationally symmetrical body.

The method described hereinbefore makes it possible to produce gloss pigments with a high production rate, having very good stability properties and being distinguished by a wide range of possible hues with good colour saturation and covering power.

The gloss pigments produced in accordance with the method according to the invention especially have a high degree of colour purity and gloss and are highly shear-stable. The pigment platelets dissolved away from the carrier have, with respect to one another, substantially identical and reproducible optical properties, such as, for example, the same

hue when viewed from a particular angle, because the thickness of the layers can be readily controlled.

The optional coating with TiO_2 can result in more intense colours and is preferably applied by precipitation by wet chemical means.

The titanium oxide layers are obtainable, for example, in analogy to a method described in DE-A-195 01 307, by producing the titanium oxide layer by controlled hydrolysis of one or more titanic acid esters, where appropriate in the presence of an organic solvent and a basic catalyst, by means of a sol-gel process. Suitable basic catalysts are, for example, amines, such as triethylamine, ethylenediamine, tributylamine, dimethylethanolamine and methoxypropylamine.

The organic solvent is a water-miscible organic solvent such as a C_{1-4}alcohol, especially isopropanol.

Suitable titanic acid esters are selected from the group comprising alkyl and aryl alcoholates, carboxylates, and carboxyl-radical- or alkyl-radical- or aryl-radical-substituted alkyl alcoholates or carboxylates of titanium. The use of tetraisopropyl titanate is preferred. In addition, acetylacetonates and acetoacetylacetonates of titanium, such as titanium acetylacetonate, may be used.

In accordance with an embodiment of the present invention, the method described in US-A-3 553 001 is used for application of the titanium dioxide layers.

An aqueous titanium salt solution is slowly added to a suspension of the material being coated, which suspension has been heated to about 50-100°C, especially 70-80°C, and a substantially constant pH value of about from 0.5 to 5, especially about from 1.2 to 2.5, is maintained by simultaneously metering in a base such as, for example, aqueous ammonia solution or aqueous alkali metal hydroxide solution. As soon as the desired layer thickness of precipitated TiO_2 has been achieved, the addition of titanium salt solution and base is stopped.

This method, also referred to as a titration method, is distinguished by the fact that an excess of titanium salt is avoided. That is achieved by feeding in for hydrolysis, per unit time, only that amount which is necessary for even coating with the hydrated TiO_2 and which can be taken up per unit time by the available surface of the particles being coated. In principle, the anatase form of TiO_2 forms on the surface of the starting pigment. By adding small amounts of SnO_2, however, it is possible to force the rutile structure to be formed. For example, as

described in WO 93/08237, tin dioxide can be deposited before titanium dioxide precipitation and the anatase form of TiO_2 can be converted to the rutile form of TiO_2 by calcinating at 800 to 900°C.

Where appropriate, an SiO_2 protective layer can be applied on top of the titanium dioxide layer, for which the following method may be used: A soda waterglass solution is metered in to a suspension of the material being coated, which suspension has been heated to about 50-100°C, especially 70-80°C. The pH is maintained at from 4 to 10, preferably from 6.5 to 8.5, by simultaneously adding 10 % hydrochloric acid. After addition of the waterglass solution, stirring is carried out for 30 minutes.

It is possible to obtain pigments that are more intense in colour and more transparent by applying, on top of the TiO_2 layer, a metal oxide of low refractive index, such as SiO_2, Al_2O_3, AlOOH, B_2O_3 or a mixture thereof, preferably SiO_2, and applying a further TiO_2 layer on top of the latter layer.

It is furthermore possible to subject the finished pigment to subsequent coating or subsequent treatment which further increases the light, weather and chemical stability or which facilitates handling of the pigment, especially its incorporation into various media. For example, the procedures described in DE-A-22 15 191, DE-A-31 51 354, DE-A-32 35 017 or DE-A-33 34 598 are suitable as subsequent treatment or subsequent coating.

The particles of the gloss pigment according to the invention can, where appropriate, be integrated into a polymer, for example obtainable by emulsion polymerisation as known *per se* in many variants for toner particles, or by incorporation into a thermoplastic or a polymer dispersion or solution.

The gloss pigments according to the invention can be used for all customary purposes, for example for colouring polymers in the mass, surface coatings (including effect finishes, including those for the automotive sector) and printing inks, and also, for example, for applications in cosmetics. Such applications are known from reference works, for example "Industrielle Organische Pigmente" (W. Herbst and K. Hunger, VCH Verlagsgesellschaft mbH, Weinheim/New York, 2nd, completely revised edition, 1995).

The gloss pigments according to the invention are goniochromatic and result in brilliant, highly saturated (lustrous) colours. They are accordingly very especially suitable for combination with conventional, transparent pigments, for example organic pigments such as, for example, diketopyrrolopyrroles, quinacridones, dioxazines, perylenes, isoindolinones etc.,

it being possible for the transparent pigment to have a similar colour to the effect pigment. Especially interesting combination effects are obtained, however, in analogy to, for example, EP 388 932 or EP 402 943, when the colour of the transparent pigment and that of the effect pigment are complementary.

The gloss pigments according to the invention can be used with excellent results for pigmenting high molecular weight organic material.

The high molecular weight organic material for the pigmenting of which the gloss pigments or pigment compositions according to the invention may be used may be of natural or synthetic origin. High molecular weight organic materials usually have molecular weights of about from 10^3 to 10^8 g/mol or even more. They may be, for example, natural resins, drying oils, rubber or casein, or natural substances derived therefrom, such as chlorinated rubber, oil-modified alkyd resins, viscose, cellulose ethers or esters, such as ethylcellulose, cellulose acetate, cellulose propionate, cellulose acetobutyrate or nitrocellulose, but especially totally synthetic organic polymers (thermosetting plastics and thermoplastics), as are obtained by polymerisation, polycondensation or polyaddition. From the class of the polymerisation resins there may be mentioned, especially, polyolefins, such as polyethylene, polypropylene or polyisobutylene, and also substituted polyolefins, such as polymerisation products of vinyl chloride, vinyl acetate, styrene, acrylonitrile, acrylic acid esters, methacrylic acid esters or butadiene, and also copolymerisation products of the said monomers, such as especially ABS or EVA.

From the series of the polyaddition resins and polycondensation resins there may be mentioned, for example, condensation products of formaldehyde with phenols, so-called phenoplasts, and condensation products of formaldehyde with urea, thiourea or melamine, so-called aminoplasts, and the polyesters used as surface-coating resins, either saturated, such as alkyd resins, or unsaturated, such as maleate resins; also linear polyesters and polyamides, polyurethanes or silicones.

The said high molecular weight compounds may be present singly or in mixtures, in the form of plastic masses or melts. They may also be present in the form of their monomers or in the polymerised state in dissolved form as film-formers or binders for surface coatings or printing inks, such as, for example, boiled linseed oil, nitrocellulose, alkyd resins, melamine resins and urea-formaldehyde resins or acrylic resins.

Depending on the intended purpose, it has proved advantageous to use the gloss pigments or gloss pigment compositions according to the invention as toners or in the form of preparations. Depending on the conditioning method or intended application, it may be advantageous to add certain amounts of texture-improving agents to the effect pigment before or after the conditioning process, provided that this has no adverse effect on use of

the effect pigments for colouring high molecular weight organic materials, especially polyethylene. Suitable agents are, especially, fatty acids containing at least 18 carbon atoms, for example stearic or behenic acid, or amides or metal salts thereof, especially magnesium salts, and also plasticisers, waxes, resin acids, such as abletic acid, rosin soap, alkylphenols or aliphatic alcohols, such as stearyl alcohol, or aliphatic 1,2-dihydroxy compounds containing from 8 to 22 carbon atoms, such as 1,2-dodecanediol, and also modified colophonium maleate resins or fumaric acid colophonium resins. The texture-improving agents are added in amounts of preferably from 0.1 to 30 % by weight, especially from 2 to 15 % by weight, based on the end product.

The gloss pigments according to the invention can be added in any tinctorially effective amount to the high molecular weight organic material being pigmented. A pigmented substance composition comprising a high molecular weight organic material and from 0.01 to 80 % by weight, preferably from 0.1 to 30 % by weight, based on the high molecular weight organic material, of an effect pigment according to the invention is advantageous. Concentrations of from 1 to 20 % by weight, especially of about 10 % by weight, can often be used in practice.

High concentrations, for example those above 30 % by weight, are usually in the form of concentrates ("masterbatches") which can be used as colorants for producing pigmented materials having a relatively low pigment content, the pigments according to the invention having an extraordinarily low viscosity in customary formulations so that they can still be processed well.

For the purpose of pigmenting organic materials, the effect pigments according to the invention may be used singly. It is, however, also possible, in order to achieve different hues or colour effects, to add any desired amounts of other colour-imparting constituents, such as white, coloured, black or effect pigments, to the high molecular weight organic substances in addition to the effect pigments according to the invention. When coloured pigments are used in admixture with the effect pigments according to the invention, the total amount is preferably from 0.1 to 10 % by weight, based on the high molecular weight organic material. Especially high goniochromicity is provided by the preferred combination of an effect pigment according to the invention with a coloured pigment of another colour, especially of a complementary colour, with colorations made using the effect pigment and colorations made using the coloured pigment having, at a measurement angle of 10°, a difference in hue (ΔH^*) of from 20 to 340, especially from 150 to 210.

Preferably, the gloss pigments according to the invention are combined with transparent coloured pigments, it being possible for the transparent coloured pigments to be present either in the same medium as the effect pigments according to the invention or in a

neighbouring medium. An example of an arrangement in which the effect pigment and the coloured pigment are advantageously present in neighbouring media is a multi-layer effect surface coating.

The pigmenting of high molecular weight organic substances with the pigments according to the invention is carried out, for example, by admixing such a pigment, where appropriate in the form of a masterbatch, with the substrates using roll mills or mixing or grinding apparatuses. The pigmented material is then brought into the desired final form using methods known *per se*, such as calendering, compression moulding, extrusion, coating, pouring or injection moulding. Any additives customary in the plastics industry, such as plasticisers, fillers or stabilisers, can be added to the polymer, in customary amounts, before or after incorporation of the pigment. In particular, in order to produce non-rigid shaped articles or to reduce their brittleness, it is desirable to add plasticisers, for example esters of phosphoric acid, phthalic acid or sebacic acid, to the high molecular weight compounds prior to shaping.

For pigmenting surface coatings and printing inks, the high molecular weight organic materials and the gloss pigments according to the invention, where appropriate together with customary additives such as, for example, fillers, other pigments, siccatives or plasticisers, are finely dispersed or dissolved in the same organic solvent or solvent mixture, it being possible for the individual components to be dissolved or dispersed separately or for a number of components to be dissolved or dispersed together, and only thereafter for all the components to be brought together.

Dispersing an effect pigment according to the invention in the high molecular weight organic material being pigmented, and processing a pigment composition according to the invention, are preferably carried out subject to conditions under which only relatively weak shear forces occur so that the effect pigment is not broken up into smaller portions.

The colorations obtained, for example in plastics, surface coatings or printing inks, especially in surface coatings or printing inks, more especially in surface coatings, are distinguished by excellent properties, especially by extremely high saturation, outstanding fastness properties and high goniochromicity.

When the high molecular weight material being pigmented is a surface coating, it is especially a speciality surface coating, very especially an automotive finish.

The Examples that follow illustrate the invention without limiting the scope thereof. Unless otherwise indicated, percentages are percentages by weight.

Example 1

A layer of about 50 nm of NaCl is vapour-deposited onto a metallic carrier in a vacuum chamber at a pressure of less than about 10^{-2} Pa. Then, at the same pressure, the following materials are successively vapour-deposited: Si, SiO and Si, as a result of which a film having the following layer structure is produced on the metal belt:

$SiO_x/SiO/SiO_x$

The separating agent is then dissolved in water, whereupon flakes come away from the substrate. At atmospheric pressure, the resulting suspension is concentrated by filtration and rinsed several times with deionised water in order to remove Na^+ and Cl^- ions that are present. That is followed by the steps of drying and, optionally, heating of the plane-parallel SiO_x structures in the form of loose material at 200°C for two hours in an oven through which air heated to 200°C is passed. On heating of the platelets, an SiO_2 layer about 20 nm thick is formed on the surface, on the SiO_x layer. After cooling, comminution and grading by air-sieving are carried out.

In accordance with the method described above, the products indicated in the following Table are obtained:

Example	$SiO_{0.2}$ [nm]	SiO_2 [nm]	$SiO_{0.2}$ [nm]	Colour	Colour change
1a	45	160	45	matt orange	matt orange to matt yellow-green
1b	45	240	45	matt blue-green	matt blue-green to matt violet
1c	45	260	45	glossy blue-green	glossy blue-green to glossy violet
1d	45	280	45	glossy green	glossy green to violet
1e	45	440	45	glossy yellow-green	glossy yellow-green to glossy green

The pigments obtained in accordance with Example 1 exhibit a colour change when the viewing angle is changed.

A pigment sublimated onto a mirror-like steel belt, having the layer sequence SiO_x (45 nm)/SiO_y(280 nm)/SiO_x(45 nm), wherein x is 0.3 and y is from 0.95 to 1.2, exhibits the

dependency of L/C/h values (standard illuminant D65; CIE31 colour coordinates) on viewing angle as indicated in the following Table.

Viewing angle (degrees)	L	C	h
10	69	59.3	343
20	71.8	50.5	351
30	76.6	38.5	13
40	81	32.8	55.6
50	83.6	42.9	89.1
60	85.2	45	102.7

Example 2:

Lipstick base having the following composition:

Number	Substance		Amount [%]
1	cera alba		11.4
2	candelilla wax		8.1
3	carnauba wax		3.8
4	Lunacera M		6.0
5	castor oil		38.8
6	Controx KS		0.1
7	aroma oil		1.0
8	Amerlate P		2.5
9	OH lan		1.6
10	isopropyl palmitate		10.1
11	Dow Corning 556		2.8
12	Dow Corning 1401		3.3
13	TiO_2 pigment		2.3
14	pigment according to Example 1a		8.2
		Total	100.0

Substances 8 - 10 are mixed together, and substances 13 and 14 are dispersed in the resulting mixture. The resulting paste is then passed several times through a three-roll apparatus. In the meantime, substances 1 - 6 are melted, stirred together until homogeneous, and then substances 7, 11 and 12 are stirred in. The two mixtures are then

mixed together in the hot state until homogeneous distribution is achieved. The hot mass is then poured into a lipstick mould and allowed to cool. Lipsticks having an intense colour of outstanding light fastness and very good gloss, and exhibiting no bleeding, are obtained.

Example 3

Nail varnish

A nail varnish has, for example, the following formulation [in %]:

methyl acetate	8.0
ethyl acetate	8.0
propyl acetate	12.0
butyl acetate	25.0
polyester resin	7.5
nitrocellulose/isopropanol	21.0
toluenesulfonamide epoxy resin	9.0
camphor	1.5
dibutyl phthalate	5.0
stearalkonium hectorite	1.0
titanium dioxide	0.6
pigment according to Example 1a	1.2
bismuth oxychloride	0.2

What is claimed is:

1. A cosmetic preparation comprising

(a) from 0.0001 to 90 % by weight of a gloss pigment comprising

(a1) a core consisting of a substantially transparent or metallically reflecting material, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95

and

(b) from 10 to 99.9999 % of a cosmetically suitable carrier material, based on the total weight of the cosmetic preparation or formulation.

2. A cosmetic preparation according to claim 1, wherein the core consists of a metallically reflecting material selected from Ag, Al, Au, Cu, Cr, Ge, Mo, Ni, Si, Ti, Zn, alloys thereof, graphite, Fe_2O_3 and MoS_2.

3. A cosmetic preparation according to claim 1, wherein the core consists of a transparent material selected from mica, SiO_z, in particular SiO_2 and SiO_2/TiO_2 mixtures, in particular SiO_2/TiO_2 mixtures, wherein $1.4 \leq z \leq 2.0$.

4. A cosmetic preparation or formulation according to either claim 2 or claim 3, wherein the gloss pigment has the following layer structure: $SiO_2/SiO_x/SiO_z/SiO_x/SiO_2$, $SiO_2/SiO_x/Al/SiO_x/SiO_2$, $TiO_2/SiO_2/SiO_x/SiO_z/SiO_x/SiO_2/TiO_2$ or $TiO_2/SiO_2/SiO_x/Al/SiO_x/SiO_2/TiO_2$, wherein x is from 0.03 to 0.95 and $1.4 \leq z \leq 2.0$.

5. A cosmetic preparation according to claim 4, wherein the gloss pigment has the following layer structure: $SiO_2/SiO_x/SiO_2/SiO_x/SiO_2$ or $TiO_2/SiO_2/SiO_x/SiO_2/SiO_x/SiO_2/TiO_2$, wherein x is from 0.03 to 0.90, preferably from 0.05 to 0.5.

6. A pigment comprising

(a1) a core consisting of SiO_z with $0.95 < z \leq 2.0$, in particular $1.4 \leq z \leq 2.0$, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95.

7. A pigment according to claim 6, wherein the pigment has the following layer structure:

(a3) SiO_2,

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95,

(a1) a core consisting of SiO_z with $0.95 < z \leq 2.0$, in particular $1.4 \leq z \leq 2.0$, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95, and

(a3) SiO_2.

8. A pigment according to claim 7 having the following layer structure

$$SiO_2/SiO_x/SiO_z/SiO_x/SiO_2 \text{ or}$$

$$TiO_2/SiO_2/SiO_x/SiO_z/SiO_x/SiO_2/TiO_2,$$

wherein x is from 0.03 to 0.95, preferably from 0.05 to 0.5 and $0.95 < z \leq 2.0$.

9. A pigment according to claim 8, wherein the thickness of the gloss pigment deviates from the average thickness of the gloss pigment by less than 10 %, preferably less than 5 %.

10. A composition comprising a high molecular weight organic material and from 0.01 to 80 % by weight, preferably from 0.1 to 30 % by weight, based on the high molecular weight organic material, of a pigment according to any of claims 6 to 9.

Abstract of the Disclosure:

The present invention relates to a cosmetic preparation or formulation comprising

(a) from 0.0001 to 90 % by weight of a gloss pigment comprising

(a1) a core consisting of a substantially transparent or metallically reflecting material, and

(a2) at least one coating substantially consisting of one or more silicon oxides, the molar ratio of oxygen to silicon being on average from 0.03 to 0.95

and

(b) from 10 to 99.9999 % of a cosmetically suitable carrier material, based on the total weight of the cosmetic preparation or formulation.